

NEXAFS of PAMAMOS Dendrimer Polymer Network-Based Nanocomposites

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Beamline(s): U7A

Introduction: Work is progressing on the development of nanocomposites using cross-linked poly(amido-amine-organosilicon) (PAMAMOS) dendrimers as the host matrix. The intent is to take advantage of functionalized dendrimer interiors that complex with an added constituent, resulting in nanocomposites using the dendrimers as templates (See Figure 1). A principal supposition in the selection of this system is that the N and O moieties contained in the dendrimer interior are highly interactive with the added metallic ions. Networks based upon radially layered copolymeric poly(amidoamine-organosilicon) (PAMAMOS) dendrimers modified with Cu^{2+} were characterized using near edge X-ray absorption fine structure (NEXAFS) spectroscopy.

Methods and Materials: Crosslinked poly(amidoamine-organosilicon) (PAMAMOS) dendrimer films were prepared from dimethoxymethylsilyl-terminated PAMAMOS dendrimers, as reported elsewhere.¹ Using an *in-situ* preparation method, a methanol solution of desired salt (e.g., CuCl_2) was added directly into the solution of precursor PAMAMOS dendrimer in the same solvent, and crosslinking was performed. Two generations (G1 and G4, as related to the number of radial layers) of precursor PAMAMOS were used. NEXAFS was performed on the samples over the energy range of 250 - 600 eV spanning the C, N, and O edges using the U7A sample station.

Results: NEXAFS partial electron yield spectra for the base dendrimer and Cu^{2+} cation-containing equivalents were obtained. Key results are:

- Electrophilic guests (Cu^{2+}) were shown to strongly chelate with both the amido N and carbonyl O within the PAMAMOS. The ester and siloxane O plays no part in the Cu^{2+} binding.
- Interaction with interior N saturates above the 9 mass % theoretical limit for Cu^{2+} in the generation four (G4) system.
- Chelating efficiency in the presence of Cl^{1-} (using CuCl_2) is much less than in the presence of SO_4^{2-} (using CuSO_4).
- Quantitative G1 versus G4 size effects were determined for N and O. A comparative result for the carbonyl O interaction with Cu^{2+} (derived from CuCl_2) is shown in Figure 2.
- The NEXAFS technique does not detect non-covalent Cu/tertiary N interaction within the PAMAMOS due to the planar symmetry of that particular moiety.

Conclusions: Previous work using electron paramagnetic resonance² left unclear which O type (carbonyl or ester) was key in the chelating of metallic cations in these systems. The NEXAFS results clearly indicate that the carbonyl O (not the ester) as well as the N moieties are responsible for the strong electrophilic interaction.

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References: 1. P. R. Dvornic et al., Ch. 16 in *Silicones and Silicone-Modified Materials*; ACS Symp. Ser. **729**, 241 (2000). 2. M. F. Ottaviani et al., *J. Am. Chem. Soc.*, **116**, 661 (1994).

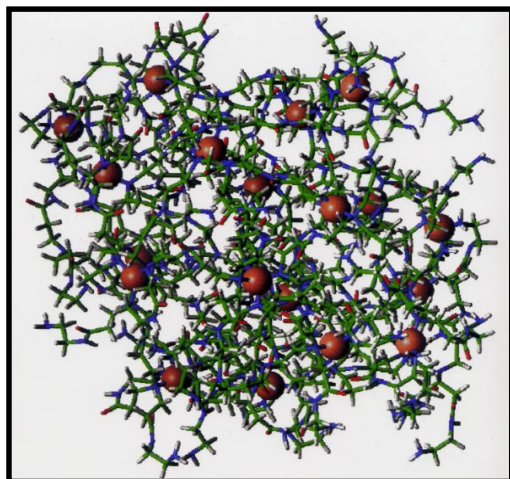


Figure 1. Molecular model of a generation 4 polyamidoamine (PAMAM) dendrimer with Cu tetracoordinated with the tertiary amines.

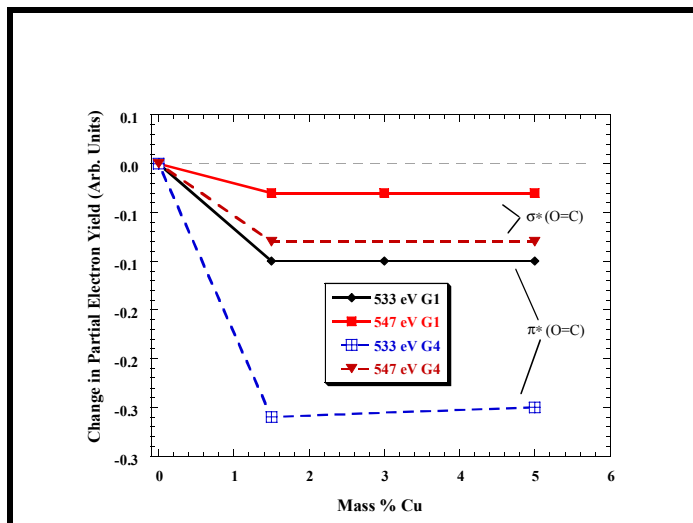


Figure 2. Change in normalized NEXAFS partial electron yield vs. mass % Cu^{2+} for the π^* and σ^* 1s electron transitions for the carbonyl O for CuCl_2 containing PAMAMOS[4,1]DMOMS G1 and G4 dendrimer polymer networks.